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Research paper

Azobenzene based 2D-MOF for high selective quinone fluorescence sensing performance

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ABSTRACT

The present work describes development of a simple and cost-effective fluorescence sensor for determination of quinone specially 1,8-dihydroxyanthraquinone (danthron). A 2D-metal-organic framework (TMU-54) containing the azobenzene group has been synthesized and applied as an efficient fluorescent sensor for danthron detection. The key feature that has a great impact on the properties of the material is the presence and distribution of functional groups within the structure. We discuss the relationship between the nature and structure of the specifically designed organic linker as well as the properties of this framework in fluorescence recognition of quinones. TMU-54 ($[Cd_3(adc)_6(DMF)_2]$) is capable of distinguishing complementary and mismatched target sequences with high sensitivity and a significant K_{sv} (1049) value.

1. Introduction

Quinones, hydroquinones, semiquinones, and their derivates have been found to undergo rapid single-electron reduction that is highly damaging to biological molecules [1,2]. Exposure of humans and wildlife to quinones and the inherent reactivity of released single-electrons may induce adverse health and toxicity effects [3,4]. Anthraquinones are also a subgroup of quinone derivatives whose study is very important because of their structural correlation with quinone antitumor drugs and anthraquinoid vat dyes [5]. On the other hand, it is all the more important as the α-hydroxy groups are present in a large number of natural anthraquinones which have found many applications in the composition of pharmaceuticals and physiologically active substances [6–8]. They are also important as dyes, analytical reagents, indicators, and in other applications. Despite this importance, few studies have been done to identify these substances and there is no report in the literature on using porous materials as sensor probes for determination of these materials [9,10].

Owing to their unique characteristics like crystalline hybrid structure, high porosity and surface area, mixed inorganic-organic nature, structural stability and designability in chemical functionality, metal-organic frameworks (MOFs) have been applied in a large variety of applications [11,12]. Perhaps the most important feature of the MOFs is their tunability through targeted selection of ligands and metal nodes for specific applications such as catalysis, sensing, and hazardous material removal [13–20]. Over the recent years, the role of functional groups in implementing various applications has been significant [21–23]. MOFs containing photoresponsive building blocks, such as azobenzene, aryl azide, and nitrobenzyl groups are currently in the spotlight due to their potential applications in different areas including molecular sensing and catalysis [24–27]. Thus, MOFs containing one of these functional groups offer a leading strategy for realizing long-range manipulation of their functions with adjustable specificity. Because of their photochemical isomerization with ultraviolet or visible light, azobenzene derivatives have been investigated as photo-switches that provide extensive geometrical changes [28,29]. Their isomerization ability could provide a significant alteration in polarity [30,31]. Due to the advantages mentioned above, in the past decade, many MOFs employed as ideal luminescent materials, have been reported for sensing of different kinds of pollutants [32]. MOFs have been applied as chemical sensors for detecting different types of analytes such as metal ions, small-molecules, volatile organic compounds, nitroaromatics, anions, and bio-chemicals. Considering their widespread release in the nature and their critical hazards on the environment and human body, detection of metal ions through MOFs has received a lot of attention over the past few years [33,34].

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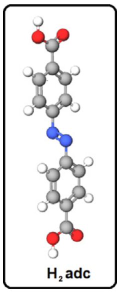

Scheme 1. Schematic presentation of azobenzene-4,4-dicarboxylic acid (adc) linker.

Luminescent metal–organic frameworks (LMOFs) have several key advantages over other luminescent probe materials [35]. The natural crystallinity of metal–organic frameworks allows exact structure determination by X-ray crystallography, providing precise information about atomic positions and the interactions that may be used in various applications. Long range interactions include radioactive energy transfer, in which target molecules absorb emissions from the probe material [36,37].

Herein, inspired by this approach, we report the synthesis of a 2D luminescent MOF containing an azobenzene group. The chosen ligand was azobenzene-4,4-dicarboxylic acid (adc) (Scheme 1) which led to synthesis of TMU-54 ($[Cd_3(adc)_6(DMF)_2]$). The sensitivity of TMU-54 towards quinone derivatives was studied in an ethanolic solution. This structure can act as a turn-off fluorescence sensor for quinones.

2. Experimental

2.1. Synthesis of the azobenzene-based ligand

The azobenzene-4,4-dicarboxylic acid (adc) linker was synthesized according to the previously reported procedure [17]. Also for more information, the synthesis has been discussed in the supporting information (Scheme 1).

2.2. Synthesis of TMU-54 ($[Cd_3(adc)_6(DMF)_2]$)

The single crystals of TMU-54 ($[Cd_3(adc)_6(DMF)_2]$) were synthesized by heating a mixture of 1 mmol adc ligand (0.27 g), 1 mmol of $Cd(NO_3)_2\cdot4H_2O$ (0.3 g) and DMF (15 mL) in a Teflon-lined stainless steel autoclave under autogenous pressure at 100 °C for 2 days. After cooling to room temperature at the rate of 5 °C h^{-1}, TMU-54 red crystals were obtained in 40% yield. m.p.: 300 °C. FT-IR data (KBr pellet, cm^{-1}): selected bands are: 673 (m), 789 (m), 1012 (m), 1388 (m), 1620 (s), 1665 (vs) and 3410 (br).

2.3. General method of quinine derivatives fluorescence sensing

All the fluorescence titrations were carried out with a 3 mg stable suspension of reported crystals in 3 mL ethanolic solution of quinolones. Excitation and emission wavelengths of the compound TMU-54 in ethanol were 370 nm and 430 nm, respectively.

It should be noted that before any sensing process, the crystal activation was done. The trapped solvent was removed by soaking the synthesized crystals in 15 mL of CH_3CN solvent for 4 days. Fresh acetonitrile was exchanged every 24 h and after 3 days the solvent was decanted. Finally, the CH_3CN was evaporated by heating the crystals at 120 °C for 24 h. The activation was confirmed by FT-IR spectroscopy

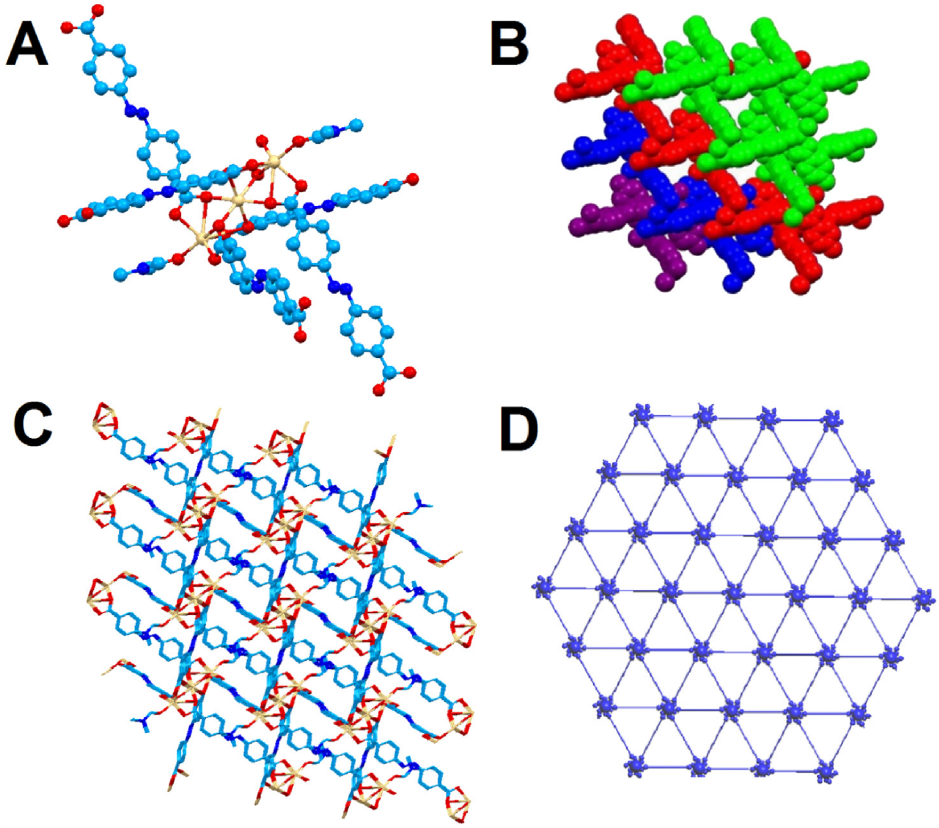

Fig. 1. Coordination environment around Cd atoms (A), separated chains of the supramolecular structure (B), 3D structure of TMU-54 (C), and simplified structure of TMU-54 (D).

(absence of the peak at 1666 cm^{-1}) and powder X-ray diffraction (stability in the crystal structure).

3. Results and discussion

3.1. Characterization of TMU-54

TMU-54, was synthesized to have a centrosymmetric triclinic space group (*P*-1). Crystal data with data collection and refinement parameters are summarized in Table S1, also selected bond distances and angles are given in Table S2. The hourglass-like $[Cd_3(COO)_6]$ SBUs of the TMU-54 ($[Cd_3(adc)_6(DMF)_2]$) contains two different Cd(II) centers in which Cd_1 is connected by six oxygen atoms (Cd_1O_6) of six different adc linkers creating an octahedral environment, while Cd_2 has seven coordinated geometry interacting with six oxygen atoms of three adc ligands and one oxygen atom from a coordinated DMF molecule. The distance between the two cadmium atoms in hourglass-like Cd_3 SBU is 3.412 Å. The three ligands attached to each Cd_1 atom are spaced apart in the space between the three ligands attached to another Cd_1 atom with opposite orientation (Fig. 1). This particular orientation and interpenetration leads to the reduction of free space in the structure. The supramolecular features of TMU-54 are controlled by weak directional intermolecular interactions. The π-π stacking interactions through isolated chains create a 3D supramolecular framework. To investigate the porosity of these structures, the Brunauer-Emmett-Teller (BET) measurements of N_2 gas were f demonstrate that TMU-54 has a surface area of 35.7 m^2/g (Fig. 2).

3.2. Thermal stability studies of TMU-54

Thermogravimetric analysis (TGA) of the TMU-54 shows the good thermal stability of the structure. The two-step gradual weight loss (in temperature range of 325–500 °C) corresponds to the decomposition of the framework (calc.: 67%, found: 65.5%) corresponding to the separation of the ligand connected to the metal node. Therefore, the structure is stable at temperatures up to 300 °C (Fig. 3 and Figs. S2–S5).

3.3. Quinoline-sensing ability of TMU-54

Owing to photophysical properties of MOFs in signal transduction and advantages of photoluminescence (PL) methods, PL-based methods have received more attention compared to other methods. PL methods are highly sensitive with reachable single molecular detection limits, easily manipulable, practical in real-life and in-field applications, with rapid response time, and able to be addressed by powdered materials directly. A very critical advantage of PL-methods is that both powder and crystal of LMOFs can be applied in metal ion detection without the need for film fabrication [35]. Therefore, considering the hybrid nature of MOFs and, they can rise to optical emission and transduce special kind of signals under photoinduced excitation conditions which is a very favorable behavior for PL-methods. Various fluorescence-based chemosensors were used for the detection of different analytes but using LMOF due to the minimum material consumption is considered cost-effective. As a result, MOF-based sensor materials have been extensively applied in photoluminescence-based methods as the most widely explored technique for detection of metal ions to date. Due to the fact that Cd^{2+} (d^{10}) is the metal used to synthesize TMU-54, the fluorescence is ligand-derived. Given the structural properties of the structure's ligands and their ability to form hydrogen bonding, electron donation of azobenzene group, and probability of π-π stacking with the guest molecule, quinone derivatives were selected as target structures for detection. Model experiments were conducted to demonstrate our assumption and evaluate the sensing ability of TMU-54 to benzoquinone, naphthoquinone, anthraquinone, phenol, and 1,8-dihydroxyanthraquinone. Stern–Volmer equation has generally been proposed to investigate the response to quenching of various analytes (see the supporting information). The results are presented in Table 1, which show that TMU-54 is a turn-off fluorescence detector for quinone derivatives. As it is shown in Table 1, the structure of TMU-54 acts as a turn-off fluorescence sensor to quinone derivatives, but does not show any particular reaction in the presence of 1,8-dihydroxyanthraquinone.

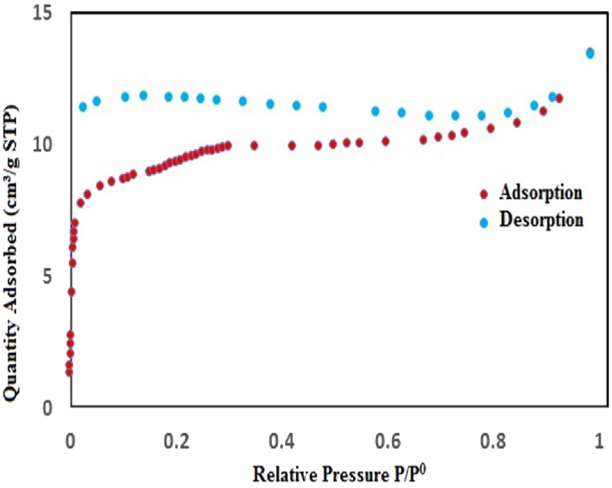

Fig. 2. N_2 adsorption–desorption isotherms of TMU-54 (B).

The order of quenching efficiency in the presence of TMU-54 is 1,8-dihydroxyanthraquinone > Naphthoquinone > 1,4-Benzoquinone > Anthraquinone (Figs. S2 and S3 and Fig. 4).

Quinones have a low-lying unoccupied π* orbital, which can accept an electron from the excited state chemophore, thus efficiently quenching the fluorescence emission of this compound but in the case of 1,8-dihydroxyanthraquinone sensing by TMU-54, the proximity of the excitation wavelength of the guest to the emission wavelength of the host justifies the observed effect. For compounds containing α-hydroxy group tautomerism involves a proton transfer along a conjugation chain from hydroxy group and adjacent carbonyl group [31]. Intermolecular hydrogen bonding as well as the π-π stacking interaction can also be effective in danthron sensing by TMU-54.

The UV–Vis spectra of all the analytes have been studied (Fig. 5). The overlap of the fluorescence emission spectrum of the sensor with the absorption spectrum of the analytes is a more important factor. When the proximity between a donor and an acceptor, with sufficient spectral overlap, is of < 10 nm the energy transfer process can be achieved. The large overlap of TMU-54 emission peak with the absorption spectrum of danthron and the lack of spectral overlap between TMU-54 and other analytes confirm the energy transfer process mechanism in 1,8-dihydroxyanthraquinone sensing by TMU-54 (Fig. 5).

The XRD patterns of TMU-54 before and after the sensing process are shown in Fig. 6. The intact patterns show that the structures remain unchanged during the sensing process (see Fig. 6).

As a result, we can clearly argue that fine tuning of MOF cavities with ideal organic functional groups can provide situations resulting in high sensing ability of MOFs despite their moderate surface areas. Considering this point, we applied azobenzene decorated TMU-54 for sensing of 1,8-dihydroxyantraquinone to take advantage of its strong and improved characteristics. Therefore, TMU-54 shows high sensitivity towards 1, 8-dihydroxyantraquinone (K_{sv} > 1040) compared with other quinone derivatives.

4. Conclusion

In this work we synthesized a fluorescent MOF (TMU-54) by the solvothermal method. The sensing ability of TMU-54 (containing the same azobenzene functional group) toward quinone derivatives was studied. The activated TMU-54 can selectively detect quinones and

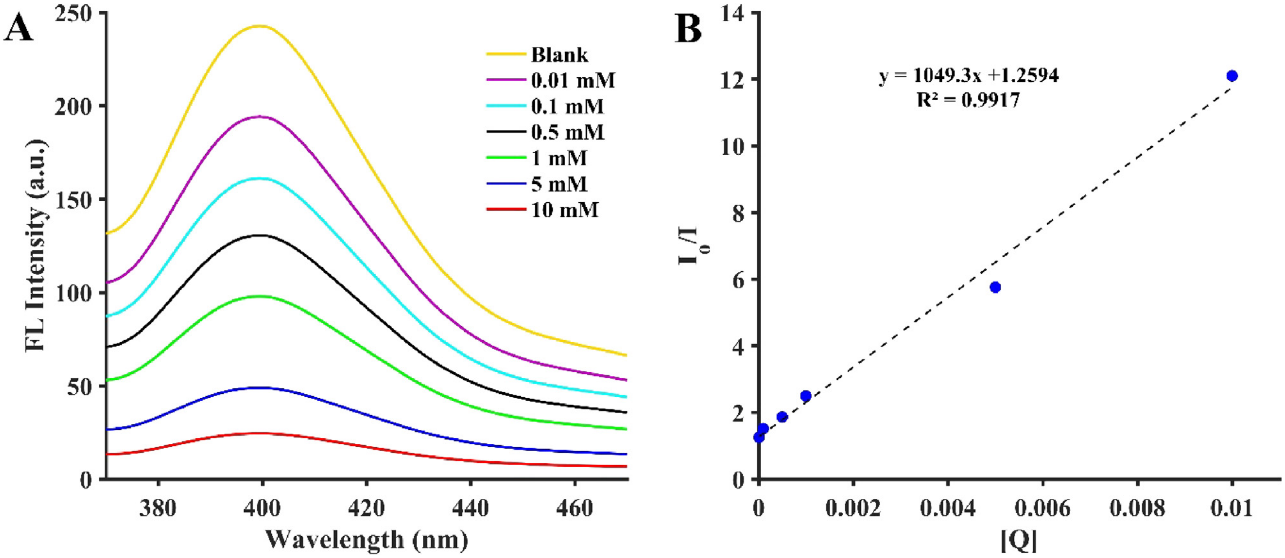

Fig. 3. Fluorescence emission spectra of TMU54 dispersed in EtOH solution of hydroxyanthraquinone at different concentrations, excited at 360 nm (b) Stern–Volmer (SV) plots in the presence of 5 mg of TMU-54 and in different concentration of 1,8-dihydroxyanthraquinone.

Table 1
The K_{sv} values (S^{-1}) obtained from quinones sensing by TMU-54.

Analyte	TMU-54
Naphthoquinone	880
1,4-Benzoquinone	248
Anthraquinone	122
1,8-dihydroxyanthraquinone	1049

especially 1,8 dihydroxyanthraquinone (danthron). Fluorescence titration experiments confirmed that TMU-54 shows selective detection towards quinones in the presence of other compounds and also demonstrates a detection limit of 1×10^{-5} M for 1,8-dihydroxyanthraquinone. On the other hand, TMU-54 can detect quinones with lower K_{sv} values, expect for anthron. Investigations reveal that Lewis basicity and electron donation of azobenzene (—C—N═N—C—) have significant effects on danthron sensing by TMU-54. This type of interaction is beneficial to such fast and sensitive detection abilities.

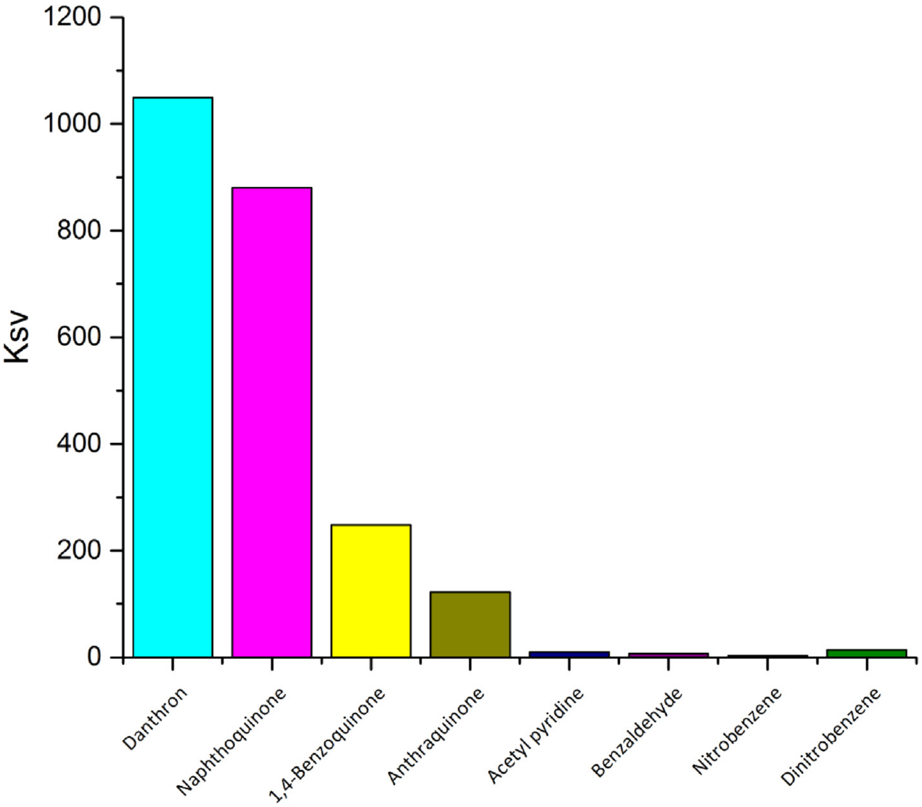

Fig. 4. Fluorescence spectra of other studied analytes, excited at 370 nm.

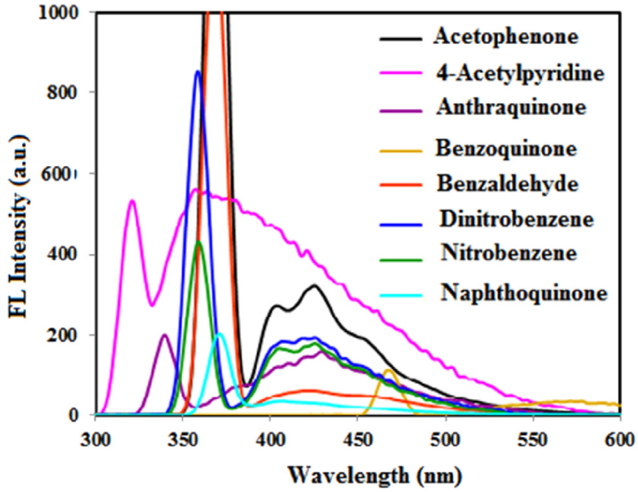

Fig. 5. Comparative Ksv of TMU-54 in different organics.

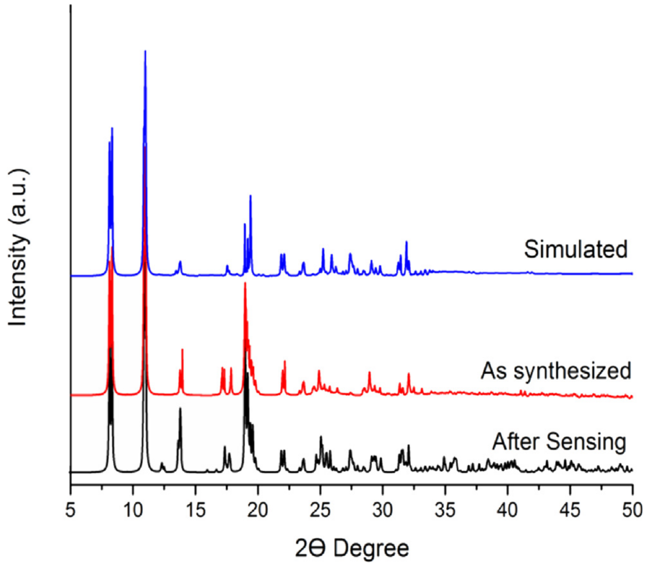

Fig. 6. Comparison of TMU-54 XRD patterns before and after the sensing process with the simulated one.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119697.

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